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Template Synthesis of Conducting Polymers - Enhanced Conductivity,
Enhanced Supramolecular Order, Interesting Microstructures

by

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TEMPLATE SYNTHESIS OF CONDUCTING POLYMERS - ENHANCED CONDUCTIVITY, ENHANCED SUPERMOLECULAR ORDER, INTERESTING MICROSTRUCTURES. C.R. Martin, Z. Cai, L.S. Van Dyke, W. Liang, Department of Chemistry, Colorado State University, Ft. Collins, CO, 80523.

INTRODUCTION

Template synthesis entails the synthesis of an electronically conductive polymer within the pores of a microporous membrane (1-5). The membranes employed have cylindrical pores of equivalent pore diameter (1-5). These pores spatially-confine the synthesis and act as templates for the resulting polymer. Conductive polymer fibrils (see Figure 1) and in some cases hollow fibrils (i.e. tubules, see Figure 2) (4) are obtained. We have used the template method to synthesize electronically conductive polymer fibrils and tubules with diameters ranging from 30 nm to 12 μ m.

Template synthesis is interesting from a variety of view points. First, this method allows for the production of polymeric micro and nanostructures with monodisperse dimensions; this is particularly important for the case of tubules since there is currently only one other known method for synthesizing organic microtubules (6). We have also shown that the conductivities of nanoscopic conductive polymer fibrils can be orders of magnitude higher than conductivities of films of the analogous polymer (3). Finally, we have shown that the nanoscopic fibrils and tubules have enhanced supermolecular order. In this paper we will discuss various aspects of template synthesis and of the fibrils and tubules obtained.

EXPERIMENTAL

Polymer Syntheses. Nuclepore polycarbonate microporous membranes were obtained from the Nuclepore Corporation (Pleasanton, CA) (1,3). Anopore alumina microporous membranes were obtained from Anotech Ltd (2,5). Polyacetylene fibrils (Figure 3) were synthesized by polymerizing acetylene within the pores (dia = 200 nm) of an Anopore filtration membrane (5). The polymerization catalyst was $\text{Ti}(\text{O}i\text{Bu})_4/\text{AlEt}_3$ (7). The Anopore membrane and catalyst solution were added to the polymerization vessel (a septum-sealed glass tube). The catalyst solution was impregnated into the pores of the host by evacuating the vessel, heating to 70° C, and then back filling with Ar. Excess catalyst was removed with a syringe. The vessel was then evacuated again and acetylene was introduced. Polymerization proceeded for 2 hours, at 0° C. The membrane was then washed in sequence with degassed toluene, 5% HCl in methanol, and pure methanol, and then dried in vacuo (5).

Polypyrrole (PPy) and poly(3-methylthiophene) tubules and fibrils were template-synthesized using the apparatus shown in Figure 4 (3,4). The Nuclepore membrane separated the monomer solution from a solution of a chemical oxidant, which served as the polymerization agent. The monomer and polymerization reagent diffuse toward each other, through the pores in the template membrane, and react to yield the polymer. We have discovered that the nascent polymer chains adsorb to the pore walls yielding a thin polymer "skin" (3,4). This "skin" becomes thicker and thicker with time, until a solid fiber is produced (3). If polymerization is quenched before this point, polymeric tubules are obtained (4).

A typical synthesis is as follows: Aqueous FeCl_3 (2 M) and aqueous pyrrole (0.3 M) were added to the outer and inner compartments, respectively, in Figure 4. The membrane used had 0.5 μ m pores. Polymerization was allowed to proceed for the desired time. If tubules were desired, short

polymerization times were employed (e.g. 25 sec). The duration of the polymerization period determines the thickness of the wall of the microtubule. If fibrils were desired, longer polymerization times (e.g. 30 min.) were used.

Conductivity (3,5) and polarized infrared absorption (5) experiments (see below) were conducted on the composite membranes; i.e. the fibrils were not removed from the Nuclepore or Anopore, host membranes. The fibrils could also be isolated by dissolution of the host membrane (3-5). Dissolution yielded a suspension of the fibrils. The fibrils were collected by filtration.

Conductivity Measurements. The conductivities of the PPy fibrils were obtained by measuring the bulk resistances of the fibril/Nuclepore composite membranes (3,5). Resistances were measured using a two-point method based on the apparatus shown in Figure 5. The upper electrode is a 0.5 mm dia. Pt wire sealed in glass. The lower electrode is a bed of 0.2 μ m-dia. Ag particles. A pressure of 1000 atm was applied between the upper and lower electrodes during the resistance measurements. This apparatus provides the bulk resistance of the composite membrane, R_c . If the composite membrane consists only of conductive polymer fibrils and intervening polycarbonate, then R_c is given

by $1/R_c = 1/R_p + 1/R_i$ where R_p is the parallel sum of the resistances of the conductive polymer fibrils and R_i is the resistance of the intervening polycarbonate. Because $R_i \gg R_p$, equation becomes $1/R_c = 1/R_p = n/R_f$ where n is the number of fibrils in the measurement area and R_f is the resistance of an individual fibril. We know from independent electron microscopic analyses (8) the exact number (n) and average size of the pores in all of the Nuclepore membrane used here. Thus, R_c provides the conductivity of a single fibril (3).

Polarized Infrared Absorption Spectroscopy (PIRAS). PIRAS is a classical method for probing for chain orientation in polymeric materials (10). PIRAS entails measurement of the absorbance, by a polymeric sample, of two orthogonally-polarized beams of IR radiation. The integrated absorption intensities for these orthogonally-polarized beams are ratioed to yield a parameter called the dichroic ratio, R (9). An R value of unity (equal absorption intensities for the two polarizations), indicates that the polymer chains are randomly oriented; a non-unity R value indicates that the chains have a preferential spatial orientation within the sample (9).

PIRAS data were obtained for the polyacetylene (PA) fibrils (5). The PIRAS experiment was conducted on the Anopore-PA composite membrane. The composite membrane was positioned at an angle of 45° with respect to the incident beam of the spectrometers. A gold wire grid polarizer was used to control the angle of polarization of the incident beam. PA was chosen for these studies because analogous PIRAS investigations have been conducted on stretched PA film (10). Stretching causes orientation of the PA chains parallel to the stretch axis and the effects of this orientation on the PIRAS data have been well documented (10).

RESULTS AND DISCUSSION.

Typical template-synthesized PPy fibrils are shown in Figure 1. Template-synthesized PPy tubules are shown in Figure 2. That template synthesis yields (initially) tubules was a completely unexpected result. Such organic microtubules have caused a great deal of excitement in the chemistry, physics, and materials science communities (6). There is currently only one other procedure for synthesizing such tubules (6). This method entails extremely expensive reagents and yields

tubules with polydisperse diameters and lengths. As indicated in Figures 1 through 3, the template method yields fibrils and tubules with monodisperse dimensions. Plots of conductivity vs. diameter for PPy fibrils are shown in Figure 6; data for two different synthesis temperatures are shown. The smallest-diameter fibrils show conductivities which are over an order of magnitude higher than the conductivity of conventional PPy film or powder (3). These are the highest conductivities ever achieved for PPy.

PIRAS data for the C-H stretching mode in the PA fibrils are shown in Figure 7 (11). In analogy to the stretch-oriented material (11), the fibrils preferentially absorb light polarized parallel to the fibril axis. An R value of 1.45 was obtained. R can be used to calculate the average orientation angle (θ) between the polymer chains and the fibril axis (11). This requires a value for the angle (α) between the transition moment of the vibration and the axis of the polymer chain (11): $\alpha=48^\circ$ for the C-H stretching mode in PA (11). A θ value of 22.5° is obtained for the PA fibrils, indicating a high degree of parallel orientation.

CONCLUSIONS

We have shown that template-synthesis yields enhanced supermolecular order and higher electronic conductivities in conductive polymers.

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Figure 1. Transmission electron micrograph of template-synthesized polypyrrole fibrils.



Figure 2. Scanning electron micrograph of template-synthesized polypyrrole tubules.



Figure 3. Scanning electron micrograph of template-synthesized polyacetylene tubules. Magnification = 1600 X.

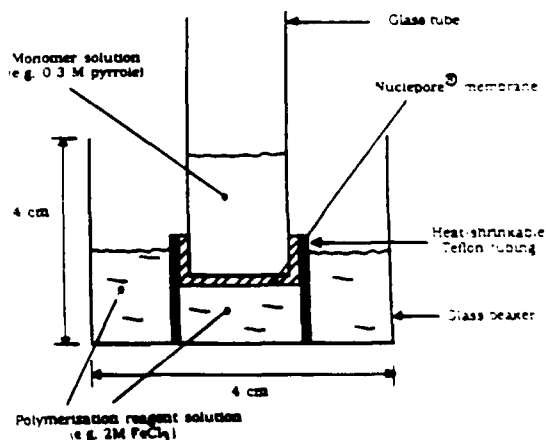
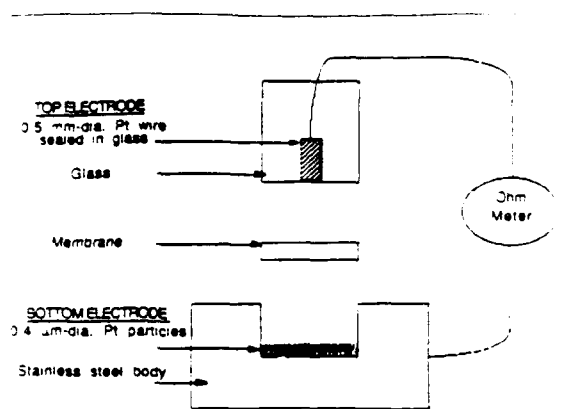


Figure 4. Schematic of apparatus used to conduct template synthesis.

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